Europäisches Patentamt | European Patent Office | Office européen des brevets

REC'D 14 DEC 2000
WIPO PCT

#2

Bescheinigung Certificate Attestation

EP 00/07174

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

4

99305908.8

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

Hatten

I.L.C. HATTEN-HECKMAN

~~DEN HAAG, DEN~~
THE HAGUE, 06/12/00
LA HAYE, LE

Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.:
Demande n°:
99305908.8

Anmeldetag:
Date of filing:
Date de dépôt:
26/07/99

Anmelder:
Applicant(s):
Demandeur(s):
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
2596 HR Den Haag
NETHERLANDS

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Breaking of oil/water emulsion

In Anspruch genommene Prioriät(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat: State: Pays:	Tag: Date: Date:	Aktenzeichen: File no. Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:
B01D17/04, C10G33/00

Am Anmeldetag benannte Vertragstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/
Etats contractants désignés lors du depôt:

Bemerkungen:
Remarks:
Remarques:

TS 0854 EPC

Crw

BREAKING OF OIL/WATER EMULSION

The invention is related to a process for breaking an emulsion of bituminous oil and water into the respective bituminous oil and water phases.

In the Orinoco Basin, in Trinidad, in North America, and in other areas, deposits of heavy oil and asphalt occur which are noted for their high bitumen content. These natural substances -which resemble oil and are commonly known as bituminous oil- can only be extracted by processes reducing viscosity and not by standard refinery methods. The extraction method currently used in the Orinoco Basin comprises emulsification of the bituminous oil at bed level, extraction of the emulsion, upgrading and transport.

Emulsifying the bituminous oils with water brings about a considerable reduction in the viscosity of these oils. The original viscosity in excess of 300 Pa.s at 20 °C is reduced to the range of 12 to 35 Pa.s as a consequence of emulsification. It is only this viscosity-reducing process that permits the extraction, transport and further processing of bituminous oil. Owing to the relatively high bitumen content, the bituminous oil cannot be easily processed by traditional refinery methods.

At present, the bituminous oil emulsion is used to fire power stations. The high sulphur content in bituminous oils (from 3 to 4%) causes a correspondingly high level of environmental pollution--a level which is becoming more and more unacceptable in the industrialised countries. The alternative is to produce desulphurized fuel gas by partial oxidation, also referred to as

downstream of the heat exchanger, like for example the gravity-type emulsion separator, must be designed for this higher pressure level for obvious safety reasons. The present invention provides a process which can be operated at a lower pressure having all the obvious advantages in view of the above.

This object is achieved by the following process. Process for separating an emulsion of a bituminous oil and water into a liquid water phase and a liquid bituminous oil phase, wherein the following steps are performed:

(a) raising the temperature of the bituminous oil/water emulsion having a temperature of below 100 °C to a temperature of above 140 °C, and

(b) performing a phase separation wherein a water phase and oil phase is obtained,

wherein the heating of the emulsion in step (a) is effected by first mixing part of oil phase obtained in step (b) having a temperature of above 140 °C with the bituminous oil/water emulsion and subsequently raising the temperature of the resulting mixture to a temperature of above 140 °C by making use of indirect heat exchange means.

It has been found that by mixing the emulsion feed with part of the bituminous oil phase obtained in the phase separation of the emulsion the temperature can be sufficiently raised in order to lower the viscosity of the mixture entering the heat exchanger means. This results in that a lower pressure drop in the heat exchanger has to be overcome enabling a lower inlet pressure. Accordingly smaller and more simple pumps, smaller heat exchanger means and process equipment designed for lower pressure levels can be used with the process according the invention.

said oil. Examples of such salts are magnesium, calcium, sodium, potassium, containing salts. Such salts may cause severe fouling in for example the process equipment of a partial oxidation process. In for example the process disclosed in US-A-5441548 the content of such water soluble salts in the bituminous oil phase will be too high for these applications. Applicants have now found that by lowering the pH of the water phase obtained in step (b) to a level of below 7 a lower content of these salts remain in the oil phase. The pH is preferably between 4 and 6. Preferably the pressure during phase separation is sufficiently high to ensure that the water phase is obtained as a liquid in step (b). Suitable pressures are between 5 and 20 bars. Obtaining the water phase as a liquid further ensures that most salts will be removed with the water phase. The improved removal of these water soluble salts by lowering the pH of the water phase is preferably used in combination with the process according to the invention. It must be appreciated that this technical measure can also be used in a more general manner and not only limited as an embodiment of the present invention in which the recycling of part of the oil is an essential feature. Typical emulsions which can be treated by the above preferred embodiment may have a calcium content of above 20 ppmw and/or a magnesium content of above 20 ppmw.

Typically the bituminous oil/water emulsion has a water phase with a pH of above 7 caused by the natural and/or the added surfactants present in the emulsion. In order to achieve the lower pH suitably an acid is added prior to phase separation. Examples of suitable acids which may be used are those acids which do not cause significant problems in the water treatment facilities in which the water phase is suitably further treated before being returned to surface water, like rivers, sea or

atoms, for example polyethoxylated tridecanol. Examples of alkali compounds are sodium chloride, potassium chloride, sodium nitrate, potassium nitrate, calcium nitrate, magnesium nitrate and mixtures thereof. The emulsion typically comprises between 60-85% by weight of the bituminous oil, between 0.01 to 5% by weight of surfactant and between 10 to 40% by weight of water. Examples of bituminous oil water emulsions optionally comprising the exemplified surfactants, which can be used in the process according to the present invention are for example described in US-A-5419852, US-A-5437693, US-A-5480583, US-A-5503772, US-A-5556574, US-A-5603864 and US-A-5622920. A preferred emulsion is Orimulsion TM as described in US-A-4795478. Orimulsion is a trademark of Intevep S.A. Venezuela.

The bituminous oil obtained in the above process can be advantageously be used as feedstock for a gasification process. The gasification process can be any process known in the art which is suitable for processing heavy feedstocks like the above described bituminous oil. Examples of such processes are the SHELL Gasification Process as for example described by Heurich et al. in "Partial Oxidation in the Refinery Hydrogen Management Scheme", AIChE 1993 Spring Meeting, Houston, 30 March 1993 and the TEXACO process as described in Petroleum Review June 1990, page 311-314. Typically the bituminous oil and oxygen or air is fed to a gasification burner. Optionally a moderator gas, for example steam or carbon dioxide, may be supplied to the burner as well. At the burner outlet the reactants are atomised and mixed and an exothermic partial oxidation takes place at a temperature of between 1300 and 1500 °C. The pressure is typically between 10 and 90 bar. The resulting fuel or synthesis gases will mainly consist of CO and H_2. Other components

(11) of the bituminous oil phase (7) is fed to gasification unit (14). To this reactor unit comprising burners (not shown) also air or oxygen is fed via (12) and optionally a moderator gas is fed via (13). The fuel gas mixture obtained via (15) is lowered in temperature in a shell-tube heat exchanger (16) to which boiler feed water is supplied to via (17) and high pressure steam (18) is generated. Fuel gas mixture (19) obtained in heat exchanger (16) is further processed in downstream unit operations (not shown) in which for example ash and soot and sulphur containing compounds are removed.

The invention will be illustrated by the following non-limiting example.

Example 1

785 ton/day of Orimulsion TM having a temperature of 40 °C was contacted with 3140 ton/day of recirculating oil phase having a temperature of 170 °C at 15 bar resulting in a mixture having a temperature of 149.5 °C. This mixture was further heated in a heat exchanger to a temperature of 170 °C having a viscosity of 179 cSt. Phase separation was performed resulting in 236 ton/day water and 3690 ton/day oil phase at 10 bar of which oil phase 3140 ton/day is used to heat the Orimulsion feed and 550 ton/day is obtained as oil product having a temperature of 170 °C and a viscosity of 102 cSt. The pressure of the circulating oil phase is raised from 10 bar to 15 bar by means of a pump. To this circulating mixture 63 kg/day of sulphuric acid is added.

Example 2

To one weight part of a typical Orimulsion TM (Orimulsion is a trade name of Intevep S.A. describing an emulsion of a bituminous oil and water and their preparation is described in US-A-4795478) an amount of sulphuric acid was added in order that the pH of the resulting water phase had a pH of 5 (80 mg sulphuric acid

CLAIMS

1. Process for separating an emulsion of a bituminous oil and water into a liquid water phase and a liquid bituminous oil phase, wherein the following steps are performed:
(a) raising the temperature of the bituminous oil/water emulsion having a temperature of below 100 °C to a temperature of above 140 °C, and
(b) performing a phase separation wherein a water phase and oil phase is obtained,
wherein the heating of the emulsion in step (a) is effected by first mixing part of oil phase obtained in step (b) having a temperature of above 140 °C with the bituminous oil/water emulsion and subsequently raising the temperature of the resulting mixture to a temperature of above 140 °C by making use of indirect heat exchange means.

2. Process according to claim 1, wherein in step (a) the temperature is raised to a value of between 140-200 °C.

3. Process according to claim 2, wherein in step (a) the temperature is raised to a value of between 160-200 °C.

4. Process according to claim 3, wherein the temperature of the resulting mixture is raised from a value of between 120-150 °C to a value of between 160-180 °C by making use of the indirect heat exchange means.

5. Process according to any one of claims 1-4, wherein the pressure in step (b) is sufficiently high in order to obtain both phases in the liquid state.

6. Process according to claim 5, wherein in step (b) the liquid water phase has a pH of below 7.

7. Process according to claim 6, wherein the pH of the liquid water phase is between 4 and 6.

A B S T R A C T

BREAKING OF OIL/WATER EMULSION

Process for separating an emulsion of a bituminous oil and water into a liquid water phase and a liquid bituminous oil phase, wherein the following steps are performed:

(a) raising the temperature of the bituminous oil/water emulsion having a temperature of below 100 °C to a temperature of above 140 °C, and

(b) performing a phase separation wherein a water phase and oil phase is obtained,

wherein the heating of the emulsion in step (a) is effected by first mixing part of oil phase obtained in step (b) having a temperature of above 140 °C with the bituminous oil/water emulsion and subsequently raising the temperature of the resulting mixture to a temperature of above 140 °C by making use of indirect heat exchange means.

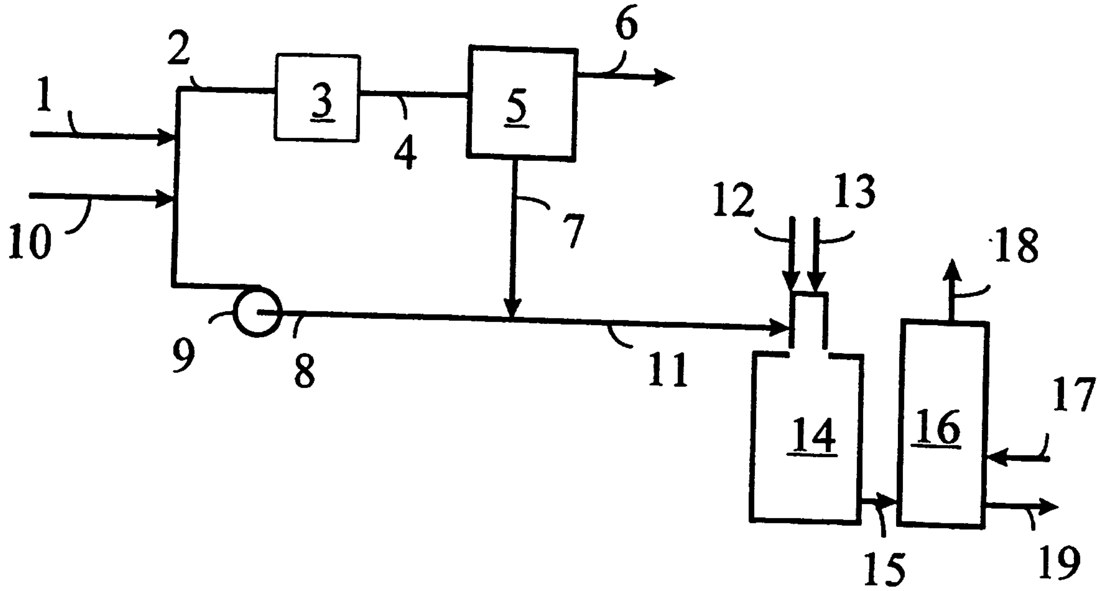

Fig. 1